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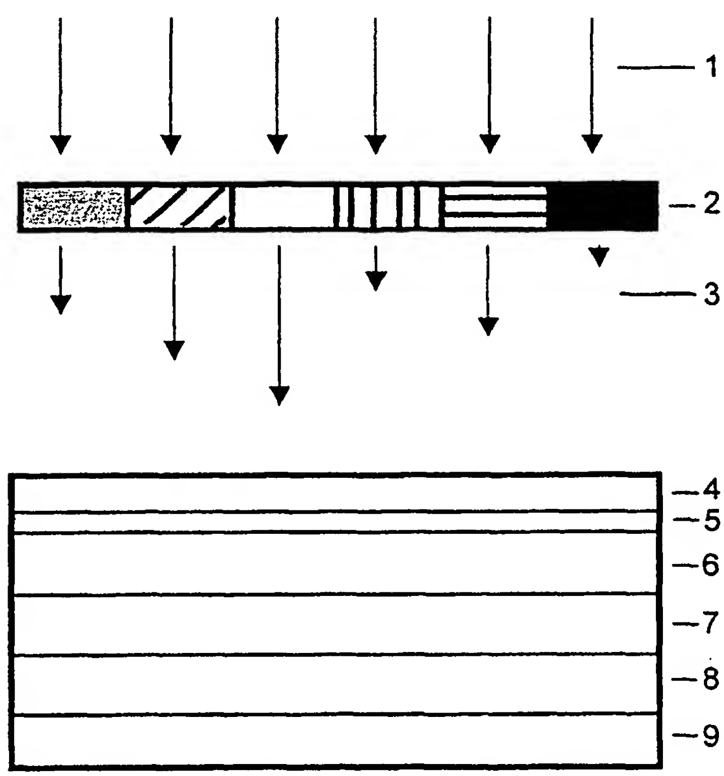
(54) Title: PATTERNED ORGANIC LIGHT EMITTING DEVICE



(57) Abstract: A method of making an electroluminescent device consisting of a layer of organic electroluminescent material between anode and cathode layers includes the step, after forming the layers on a transparent substrate, and after encapsulation of the device in a hermetically sealed packaage containing an inert atmosphere, of patterning the device using ultraviolet light. The device is exposed to ultraviolet light through a mask which is the negative of the desired pattern for the electroluminescent device. Areas of the device which receive ultraviolet light do not luminesce as brightly as areas which are shielded from the ultraviolet light. After exposure to the ultraviolet light, the device can be coated with an ultraviolet barrier layer, or placed in a structure which shields it from ultraviolet barrier layer, or placed in a structure which shields it from ultraviolet light thus preventing further degradation of the electroluminescent properties.

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Patterned Organic Light Emitting Device

Background

Organic light emitting diodes (OLED) or organic electroluminescent devices have great potential as a flat panel display technology. OLEDs are emissive devices that are flat, thin, have good viewing angle, and have the potential to be low cost.

A simple way of making an organic light emitting device (OLED) is to sandwich a light emitting material between an anode and a cathode. At least one of the electrodes needs to be transparent. It is common for a hole transporting layer (HTL) and an electron transporting layer (ETL) also to be sandwiched between the respective electrodes and the light emitting layer..

An OLED display capable of showing different images requires separately addressable pixels or segments. In a conventional pixellated display the matrix of pixels is made by structuring the electrodes into rows and columns. Even for a display showing a fixed image, the image is defined by structuring the electrodes and / or the emissive layers. The electrodes must be patterned so that electrical contact can be made to each segment. Typically the electrode in contact with the substrate can be patterned by, say, photolithography. The top electrode is commonly deposited by evaporation through a shadow mask to form the necessary pattern. However the use of a shadow mask limits the resolution, high resolution is difficult, and can be time consuming if accurate mask alignment is required. In these conventionally pixellated displays, appropriate electronic drive circuits are required to obtain grey scale, which adds to the complexity of the display.

However, for some applications, the OLED only needs to show a single fixed image. The single image may be a logo or icons; and possible uses include advertising or backlights for liquid crystal displays (LCDs). For these simple devices, it would be

desirable to have a quicker and easier way of generating a pattern. It would be even more desirable if that single pattern could have grey scale.

For OLEDs based on polymeric materials, rather than small molecule materials, some attempts have been made to pattern the light emitting layer by exposing it to UV light. Usually after exposure of the precursor or polymer to UV light, the method involves washing material away, which is an additional step not needed in the current invention. In all the previous methods, (e.g. Philips US 5902689) the light emitting polymer was exposed to UV light during an intermediate step, before the cathode was deposited. In the present invention patterning is carried out after the device has been made and encapsulated. The current invention allows separation of the device manufacture and image imprinting. The current invention also has the advantage that it allows grey-scale images to be formed.

It is an aim of this invention to provide an OLED which has patterned light emission without the need to structure the electrodes.
It is a further aim of this invention to provide an OLED which has a range of brighter and darker emissive regions, without the need to structure the electrodes.
It is an aim of this invention to provide a simple method of producing a fixed pattern on an OLED device.

Summary of the Invention

This invention comprises a way of making an OLED device and then exposing portions of the device to UV light for a period, so that when subsequently operated the OLED light emission is patterned. The pattern of the light emission is higher resolution than the pattern of the electrodes.

This invention comprises a way of making an OLED device and then masking portions of the OLED with the desired pattern, and exposing the masked display to

UV light for a short time. When the OLED is switched on, by passing a current through the organic layers, the regions that were exposed to UV light do not emit as much light as the regions that were not exposed to UV light. The total amount of UV light (determined by the intensity and the exposure time) that falls on an area determines how much light the area subsequently emits. A suitable mask patterned to vary the amount of UV falling on different areas of the OLED allows grey-scale images to be produced.

In more detail, an aspect of the invention provides a method of making an electroluminescent device comprising the steps of:

forming the electroluminescent device;

encapsulating the device in an inert atmosphere to form a hermetically sealed package; and

after the encapsulation step, exposing the device to ultraviolet light to reduce the emissivity of the device.

The step of exposing the device to ultraviolet light may comprise selectively exposing areas of the device to ultraviolet light to reduce the emissivity of those areas, such that when the device is energised a pattern consisting of variations in luminescence is created, for instance by exposing through a mask having regions which attenuate the ultraviolet light, the regions forming a pattern which is the negative of the desired pattern. The regions may attenuate the ultraviolet light by different amounts.

After exposing the device to ultraviolet light, the device may be protected from ultraviolet light, eg by coating surfaces of the device which are non-opaque to ultraviolet light with a coating which is opaque to ultraviolet light, or by encasing the device in a structure which is opaque to ultraviolet light.

The structure may comprise a liquid crystal display behind which the device is placed.

The step of forming the electroluminescent device may comprise the step of: disposing an electroluminescent substance between an anode and a cathode, eg by forming one of the cathode and anode as a layer on a substrate, forming thereon a layer of the electroluminescent substance, and subsequently forming the other of the cathode and anode as a layer thereon. A hole transporting layer may be disposed between the anode and the electroluminescent layer, an electron transporting layer may be disposed between the cathode and the electroluminescent layer, and/or an electron injecting layer may be disposed between the cathode and the electron transporting layer.

The substrate may be transparent. The step of encapsulating the device may comprise hermetically sealing a lid to the substrate.

The electroluminescent device may comprise a molecular organic or organometallic light emitting material to provide the electroluminescence.

Brief Description of the Drawings

A number of embodiments of the invention will now be described, by way of example only, with reference to the accompanying Figures, in which:-
Figure 1 shows a cross section of a masked OLED device undergoing UV irradiation;
Figure 2 shows a cross section of an operating OLED patterned according to the current invention;
Figure 3 shows a top view of an operating OLED device patterned according to the current invention.

Detailed Description of the Invention

With reference to Figure 1, a typical OLED is formed on a transparent substrate (4), onto which is deposited a transparent electrode (5), the light emitting layer (7), and finally a top electrode (8). The transparent substrate is preferably glass, but may alternatively be a transparent plastic such as PET. In a common configuration the transparent electrode is the anode, and is preferably ITO or another suitable material.

Often optional hole injecting or transporting layer(s) (6), such as triarylamine derivatives including (N,N'- Bis(napthalen-2-yl)-N,N'-bis(phenyl)benzidine) (α-NPD) or PEDOT, are deposited on the anode before laying down the light emitting layer. The light emitting layer (7) can be any known in the art, including aluminium tris(8-hydroxyquinolate) (Alq_3) optionally doped with dye, organolanthanide complexes (e.g. WO 98/55561) , or light emitting dendrimers (e.g. WO 99/21935). An optional electron transporting layer (8), such as Alq_3 or a triazole derivative, can be deposited on the light emitting layer. The cathode (9) is typically a low work function metal such as Ca, Mg, Al or an alloy such as MgAg. As known in the art, there may additionally be an electron injecting layer of, for example, LiF deposited before the Al cathode. In this configuration, light is emitted through the transparent substrate, and the OLED is viewed from that side.

Alternatively the OLED can be built on an opaque substrate, such as silicon, and viewed from above, through the top, transparent electrode.

Once the active layers have been deposited the OLED can be encapsulated in an inert atmosphere, which prolongs the useful life of the device. Commonly encapsulation involves sealing a lid onto the substrate, thereby forming a hermetic package.

In this invention, once the OLED has been made and encapsulated, a mask (2) is placed close to or in contact with the OLED, on the side from which light is emitted.

The mask should be the negative of the desired image. Areas of the mask that transmit UV light will result in dark areas on the OLED.

A simple mask can be made from metal, photographic emulsion or other materials that are opaque to UV light. Cutting out areas of the opaque mask to allow UV light onto the OLED will give the corresponding binary image.

Alternatively the mask can be made from a material that is transparent to UV light, but with areas of the mask darkened to block the UV light. The degree of darkening controls the amount of UV light reaching the OLED. The grey-scale in the negative image mask is reflected in the corresponding positive image on the OLED. These masks are effectively photographic negatives. A simple way of producing such a mask is to print an image onto a transparent acetate or other suitable film. The higher the density of ink on the film, the less UV light reaches the OLED.

Referring to Figure 1, uniform UV light (1) is incident on the mask (2). The different shading of areas of the mask (2) represents areas with different UV transmission. The intensity of the transmitted UV light (3) has the corresponding pattern to the mask, and is incident on the OLED. Referring to Figure 2, this shows the cross section of the resulting device in operation. The emitted light (10) is shown schematically by arrows, where the different length arrows represent different intensities of emitted light from the different areas. The longer the arrow the more intense the light emission. The pattern of light emission is the negative image of the mask. The dark area of the mask, which had the least UV transmission, is the brightest area of the display. Figure 3 shows a top view of the operational device. The mask was a series of stripes, with the cross section shown in Figure 1. The different shaded areas, represent areas of different intensity, with the intensity of the emitted light decreasing from area (10a) to area (10f).

The OLED is exposed to the patterned UV light for a short time. The exposure time depends on the intensity and wavelength of the light and the effect required, but typical exposure time ranges from a few seconds to several minutes, and preferably the exposure time is less than 20 minutes, more preferably less than 10 minutes and often less than 1 minute. The intensity of the UV light is preferably in the range 10 mW/cm^2 to 0.01 mW/cm^2, more preferably 1 mW/cm^2 to 0.1 mW/cm^2.

The wavelength of the UV light should be in the absorption region of at least one of the organic materials in the OLED. A mercury lamp is a suitable source of UV with principle emission lines at 365nm, 302 nm and 254nm, but other wavelengths may also be used. For an OLED containing NPD and Alq_3 the 302nm line is preferred. If high resolution images are required the light source should be collimated and imaging optics may be used as in photolithography.

In the typical OLED configuration, the UV light needs to pass through the transparent substrate to have effect on the organic materials. The substrate may have a cut off wavelength below which it is not sufficiently transparent to UV, which will affect the choice of UV wavelength. Particularly at shorter wavelengths, a thin substrate that absorbs less UV than a thick substrate, may be advantageous, allowing a shorter exposure time to be used. This will be particularly true in the case of plastic substrates.

Once the image has been printed onto the OLED, it may be desirable to coat the transparent substrate with a UV blocking film to prevent further, potentially damaging, exposure to UV during use. Alternatively the OLED may be used in such a way that it is already afforded protection from UV light, for example as a backlight behind a liquid crystal display (LCD).

The following examples further illustrate the invention.

Example 1

A specific embodiment of this invention would be as follows:

A glass substrate measuring 30mm x 38mm and 0.4mm thick with an ITO coating of thickness 140 nm on one side is crudely etched using hydrochloric or hydrobromic acid to remove the ITO from a small region 6mm x 5mm at one corner of the backlight. This is necessary to avoid shorting between the ITO anode and the metal cathode. The overlap between the cathode and the anode defines the light emitting area of 16mm x 27mm.

A wet cleaning process is carried out using Decon 90 and de-ionised water and a final dry oxygen plasma clean at a power of 60 watts for 4 minutes is carried out just prior to evaporation. The substrate is masked and placed in an evaporator where the pressure is reduced to below 10^{-6} mbar. 40 nm of NPD (N,N'- Bis(napthalen-2-yl)-N,N'-bis(phenyl)benzidine) is evaporated at a temperature of 250°C and at a rate of 1.5 Å/s followed by 60 nm of Alq_3 (*tris* (8-hydroxyquinoline) aluminium) at a temperature of 200°C and a rate of 2 Å/s. The mask is then changed to form a cathode with a connection pad and no direct shorting routes. The cathode is deposited by evaporating 1.5 nm of LiF at a rate of 0.2 Å/s, followed by 100 nm of aluminium evaporated at a rate of 1 Å/s.

The device is encapsulated at this stage, for instance by using an epoxy gasket around the edge of the emissive area and a glass or metal plate. This procedure must be carried out in an inert atmosphere such as dry nitrogen to ensure that the cell formed by the device and cover plate contains minimal moisture and oxygen. The epoxy may be a room temperature curing epoxy or a U.V. curing epoxy, in which case the device should be illuminated from the cathode side to avoid exposure of the emitting area. The gasket should be around the edge of the device and should not encroach onto the emitting area.

In order to form the desired fixed image on the device a mask with the image in negative contrast is required. This is formed on a transparent film with grayscale if required. The mask is positioned on the side of the device with the transparent anode and this is then exposed to 0.3 mW/cm^2 of 302 nm wavelength light for 10 minutes. When the device is then driven at a constant voltage of 4.5 volts the image is visible and as the voltage is increased the image gets brighter without noticeable degradation in the contrast ratio. The image does not saturate at high drive voltages.

Example 2

A device was prepared in exactly the same way as in example 1, except that the following organic layers were deposited on the cleaned ITO: 25 nm of NPD evaporated at a rate of 1.5 Å/s, 25 nm of terbium *tris*(1-phenyl-3-methyl-4-(trimethylacetyl)pyrazol-4-one) triphenylphosphine oxide, and 25 nm of Alq_3. As in example 1 the cathode consisted of 1.5 nm of LiF and 100 nm of Al and an image was formed on the device by exposure to UV light. The image was visible in the green emission at 4.8 volts.

In both examples the epoxy used in encapsulation is a UV-curable adhesive called XNR5516-c1 from Nagase Chemtex Corporation. The curing is achieved with application of UV light at a level of 10 mW/cm^2 for 5 minutes, which is equivalent to 3000 mJ/cm^2 = 3 J/cm^2.

H_2O levels in the glovebox during the encapsulation procedure are between 1 and 4 ppm; always less than 5 ppm.

The desiccant packs are from SAES Getters and are described as GDO tablets (small). The tablets contain more than 50 mg of Calcium Oxide and three are used per backlight device. They are stuck to the inside of the can using 3M 966 tape.

The encapsulation cans are made of brass with a 1 mm lip all round for sealing to the substrate. The cans are 0.7 mm deep and, with the addition of the floor thickness of the can (0.2mm), give a total depth of 0.9 mm over the substrate thickness. The volume inside the can is (0.7 x 35 x 25) 612.5 mm^3.

CLAIMS

1. A method of making an electroluminescent device comprising the steps of:

   forming the electroluminescent device;

   encapsulating the device in an inert atmosphere to form a hermetically sealed package; and

   after the encapsulation step, exposing the device to ultraviolet light to reduce the emissivity of the device.

2. A method according to claim 1 wherein the step of exposing the device to ultraviolet light comprises selectively exposing areas of the device to ultraviolet light to reduce the emissivity of those areas, such that when the device is energised a pattern consisting of variations in luminescence is created.

3. A method according to claim 2 wherein the device is exposed to the ultraviolet light through a mask having regions which attenuate the ultraviolet light, the regions forming a pattern which is the negative of the desired pattern.

4. A method according to claim 3 wherein the regions attenuate the ultraviolet light by different amounts.

5. A method according to any one of the preceding claims, further comprising the step, after exposing the device to ultraviolet light, of protecting the device from ultraviolet light.

6. A method according to claim 5 wherein the step of protecting the device from ultraviolet light comprises coating surfaces of the device which are non-opaque to ultraviolet light with a coating which is opaque to ultraviolet light.

7. A method according to claim 5 wherein the step of protecting the device from ultraviolet light comprises encasing the device in a structure which is opaque to ultraviolet light.

8. A method according to claim 7 wherein the structure comprises a liquid crystal display behind which the device is placed.

9. A method according to any one of the preceding claims wherein the step of forming the electroluminescent device comprises the step of:

disposing an electroluminescent substance between an anode and a cathode.

10. A method according to claim 9 wherein the step of disposing an electroluminescent substance between an anode and a cathode comprises: forming one of the cathode and anode as a layer on a substrate, forming thereon a layer of the electroluminescent substance, and subsequently forming the other of the cathode and anode as a layer thereon.

11.. A method according to claim 10 wherein a hole transporting layer is disposed between the anode and the electroluminescent layer.

12. A method according to claim 10 or 11 wherein an electron transporting layer is disposed between the cathode and the electroluminescent layer.

13. A method according to claim 12 wherein an electron injecting layer is disposed between the cathode and the electron transporting layer.

14. A method according to any one of claims 10 to 13 wherein the substrate is transparent.

15. A method according to any one of claims 10 to 14 wherein the step of encapsulating the device comprises hermetically sealing a lid to the substrate.

16. A method according to any one of the preceding claims, wherein the electroluminescent device comprises a molecular organic or organometallic light emitting material to provide the electroluminescence.

FIGURE 1

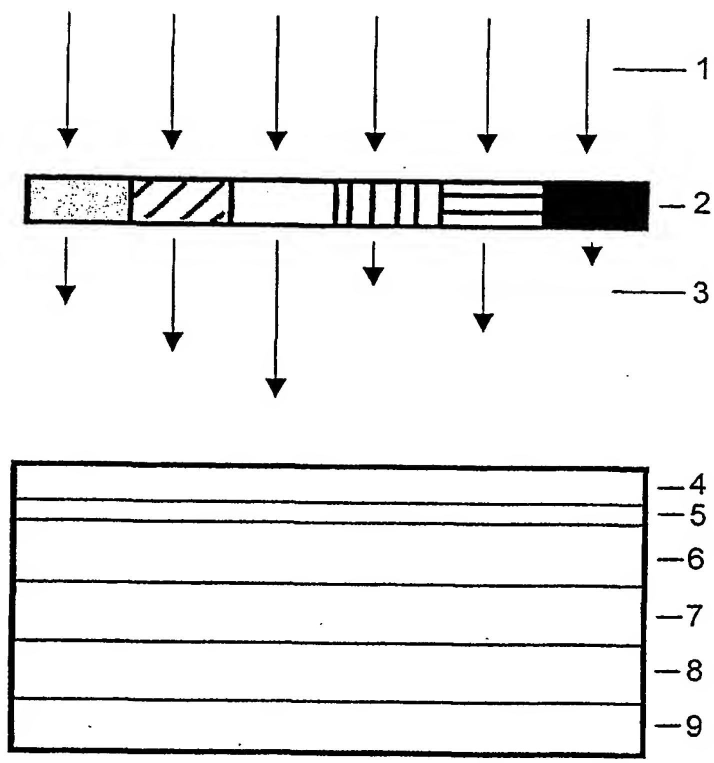


FIGURE 2

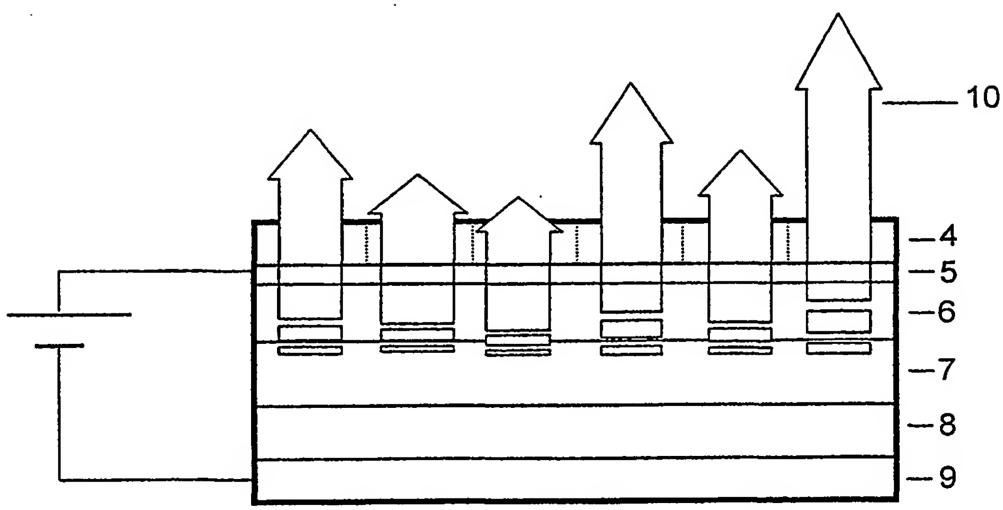
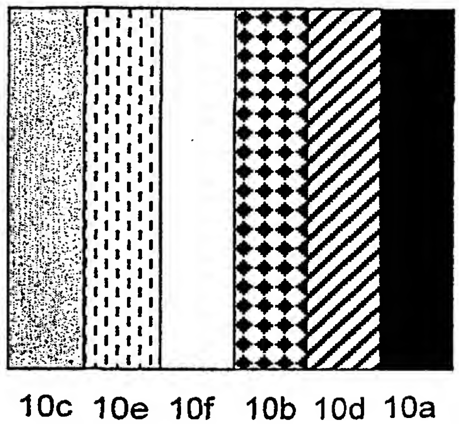


FIGURE 3



INTERNATIONAL SEARCH REPORT

Inte[rnati]onal Application No
PCT/GB 01/03190

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/40 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 06223 A (PHILIPS ELECTRONICS NV) 20 February 1997 (1997-02-20) cited in the application the whole document ---	1-5,7, 9-16
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 035 (E-1310), 22 January 1993 (1993-01-22) -& JP 04 255692 A (IDEMITSU KOSAN CO LTD), 10 September 1992 (1992-09-10) the whole document ---	1-5,7, 9-16
A	HIRAMOTO M ET AL: "Patterned emmision in organic EL device" JAPANESE JOURNAL OF APPLIED PHYSICS, 1996, vol. 35, pages 4809-4812, XP000735405 ISSN: 0021-4922 the whole document ---	1-5,16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
22 October 2001	05/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	van der Linden, J.E.

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HASEGAWA N ET AL: "Reversible EO switching of a memory type PDLC" LIQUID CRYSTALS, LONDON, 1996, vol. 21, pages 765-766, XP000639771 ISSN: 0267-8292 the whole document	1,9,10, 14
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INTERNATIONAL SEARCH REPORT

nformation on patent family members

Inte onal Application No
PCT/GB 01/03190

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